

DRAWINGS ATTACHED

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(54) MANUFACTURE OF PHENOLS

(71) We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800, North Lindbergh Boulevard, St. Louis, 66, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of phenols and more particularly to a new and improved non-catalytic process for the preparation of phenols by direct synthesis from aromatic hydrocarbons and oxygen-containing gases.

The term "phenols" is used herein to mean not only phenol itself (C_6H_5OH) but aromatic compounds generally which contain a phenolic hydroxyl group.

The phenols are a very valuable class of compounds. Phenol, as well as the cresols, thymol, carvacol and the other phenolic compounds has pronounced germicidal action and is useful as a disinfectant. In addition the phenols are useful in preparing phenolic resins, in metal cleaning compounds, and in many other applications.

Phenols may be obtained by a number of methods. Since the phenols occur in coal tars and in petroleum crude oils, phenols may be recovered from these natural sources. In addition, phenols may be synthesized from sodium benzene sulphonates and by the hydrolysis of halobenzenes.

It is an object of the present invention to provide a new and improved process for the manufacture of phenols.

According to the present invention there is provided a process for the manufacture of phenols which comprises subjecting a gaseous mixture of an aromatic hydrocarbon and a free oxygen-containing gas to a silent electric discharge. By the term "silent electric discharge", as used herein, is meant an electrical discharge of the silent type characterized by a relatively high voltage, a relatively low

current density and a relatively low gas temperature as contrasted to the low voltage, high current, and high temperatures of the arc discharge.

The feed materials to the process of the present invention consist of an aromatic hydrocarbon and an oxygen-containing gas. Most often, the aromatic hydrocarbon and the oxygen-containing gas are employed in amounts such as to produce a molar ratio of aromatic hydrocarbon to oxygen within the range of 0.1:1 to 10:1. However, both higher and lower ratios may be used if desired. Since formation of the phenol from the aromatic hydrocarbon and oxygen generally requires 1 mol of each of the reactants, it is usually preferred to employ the aromatic hydrocarbon and the oxygen-containing gas in amounts such as to produce a molar ratio of aromatic hydrocarbon to oxygen within the range of 0.1:1 to 2:1, preferably substantially equal molar quantities being used.

The oxygen-containing gases may be employed in carrying out the process of the present invention, include virtually any of the gaseous materials containing oxygen in a form which may be used in the reaction embodied in the present process. Generally, such oxygen-containing gas is one selected from the group consisting of air, oxygen, and air-oxygen mixtures. Because of its cheapness and ease in handling, air is usually preferred as the oxygen-containing gas employed in carrying out the process of the present invention.

A wide range of aromatic hydrocarbons may be used in the process of the present invention. The aromatic hydrocarbons may be mono-nuclear or poly-nuclear and may have one or more hydrocarbon substituent therein. Included within the aromatic hydrocarbons are such compounds as benzene, toluene, the xylenes, ethyl benzene, methyl ethyl benzene, n - propyl benzene, isopropyl benzene, n - butyl benzene, n - pentyl benzene, ethyl propyl benzenes, naphthalene, methyl naphthalenes, dimethyl naphthalenes, methyl ethyl naphthalenes, ethyl naphthalenes, diethyl naph-

thalenes, dipropyl naphthalenes, anthracene, phenanthrene, methyl anthracene, methyl phenanthrene, dimethyl anthracene, diphenyl and methyl diphenyl. As a practical matter, it is generally preferred to practice the process of the present invention employing aromatic hydrocarbons of relatively low molecular weight. This results from the difficulty of vaporizing the higher molecular weight aromatic hydrocarbons. In the preferred practice of the present invention, the aromatic hydrocarbons employed are benzene, toluene, ethyl benzene, the xylenes, or combinations of these.

The residence time of the oxygen-containing gas and aromatic hydrocarbons within the high intensity electric field produced by the silent electric discharge most often is within the range of 0.1 to 1000 seconds. Preferably, however, this residence time is within the range of 1 to 100 seconds. The reaction conditions of temperature and pressure at which the process of the present invention is operated vary considerably and are not particularly critical to the operation of the present invention except as hereinafter discussed. With respect to temperature, no higher temperatures are necessary than are required to maintain the aromatic hydrocarbon feed in the reaction zone in the vapor phase. As a practical matter, temperatures above 600°F seldom are used in the operation of the process of the present invention. Generally, the temperatures employed are within the range of 20 to 200°F. With regard to pressure, the operation of the process of the present invention is most often within the range of from approximately atmospheric pressure to 50 psig. However, both higher and lower pressures, i.e., 1 mm Hg to 100 psig, may be used if desired. The choice of pressure for operation of the present invention must take into consideration that the aromatic hydrocarbon employed in the present process is in the vapor state.

The electrical conducting media through which the silent electric discharge is generated may consist of any material which may act as an electrode. Such materials are well known to the art and include various metals such as the aluminum foil mentioned below or various electrolytic solutions such as the below-mentioned sodium sulfate solution. The two electrical conducting media used may be the same or different depending upon the configuration and construction of the apparatus used in carrying out the process of the present invention. Since materials and electrolytic solutions capable of conducting electricity and of acting as electrodes are well known to the art, no further discussion of such conducting media is believed necessary.

An insulating medium is required between the two electrodes employed in providing the silent electric discharge of the process of the present invention. In the apparatus shown in

the accompanying drawing (discussed in detail later herein) this insulating medium is provided by glass tubes 15 and 16 which each provide a layer of glass between the electrodes. It is not necessary that the electrodes be insulated from one another by two layers of insulation as in the apparatus of the drawing. It is only necessary that one insulating medium be provided and the reactants may be in direct contact with one of the electrodes. The choice of the insulating medium is not critical and is well within the ability of those skilled in the art. It is only necessary that the insulating material have a dielectric greater than that of the gaseous reactants. Included within this group of insulating materials are such materials as glass and various ceramic materials.

In providing the silent electric discharge of the process of the present invention, a field strength voltage from about 20,000 to about 150,000 volts per centimeter most often is required. "Field Strength", as used herein, is the value obtained by dividing the voltage applied to the electrode by the distance between the two electrodes and is a measure of the electromotive force within the reaction zone. The field strength required will vary somewhat with the residence time and the reactants involved, as well as the efficiency of contact of the reaction mixture with the high intensity electric field. A preferred field strength for operation of the process of the present invention is one within the range of 80,000 to 120,000 volts per centimeter. Generally, the frequency of the electric current in the operation of the process of the present invention is within the range of 30 cycles to 2 megacycles per second. However, a frequency within the range from 30 to 90 cycles per second is preferred.

The apparatus used in carrying out the process of the present invention may vary considerably. Any apparatus which provides a silent electric discharge across a gap through which the reaction mixture of the present process may be passed will suffice. The gap between the electrodes may vary considerably in distance and is not critical so long as a silent electric discharge of the proper strength can be obtained. This distance will vary from a small fraction of an inch to several inches and higher. The optimum gap distance will vary with the electrodes used and other considerations well within the ability of those skilled in the art. A useful apparatus is one of the general configuration illustrated by the accompanying drawing.

Referring to the drawing, an oxygen-containing gas and an aromatic hydrocarbon are fed through lines 10 and 11, respectively, into a common line 12 wherein these components become intimately mixed. The mixture passes through line 12 into one or a plurality of distributing tubes 13 which serve to intro-

duce the mixture into reaction chamber 14. The mixture is in the gaseous state on introduction into the reaction chamber. Reaction chamber 14 is formed by the annular space between a glass outer tube 15 and glass inner tube 16, which glass inner tube 16 is sealed at its lower end and filled with an electrolyte solution 17 which may be any suitable conducting solution. Glass outer tube 16 is surrounded by a conducting material 19 usually as a sheet of a conducting metal such as, for example, aluminium foil. Electrolyte solution 17 and conducting metal 19 are connected by means of conducting wires 18 and 29, respectively, with an electrical power source (not shown). The electrical power source is one capable of supplying as high as 20,000 volts and higher of alternating current with a frequency range of 30 cycles to 2 megacycles per second to electrolyte solution 17 and conducting metal 16. The gas mixture introduced through lines 13 into reaction chamber 14 passes downward through reactor chamber 14 and a high intensity electrical field created by a silent electrical discharge between electrolyte 17 and conducting material 19. The effluent of reaction chamber 14 is discharged through discharge tube 21 whereby it flows to a recovery system (not shown).

To further describe and to specifically illustrate the process of the present invention, the following examples are presented. These examples are not to be construed as limiting of the present invention.

EXAMPLE I

Benzene and air were mixed in a molar ratio of 1:8.5, benzene to air, and subjected to a silent electrical discharge in an apparatus substantially as shown in the accompanying drawing. In this apparatus, aluminum foil was used as conducting material 19 surrounding outer tube 15 and a 1% Na_2SO_4 solution was used as electrolyte 17. The distance between conducting material 19 and electrolyte 17 was 0.1 centimeters. The benzene-air mixture was subjected to the silent discharge at essentially atmospheric pressure and at a temperature of about 80°F. The voltage applied to the silent electric discharge was approximately 10,000 volts and the frequency of the applied electromotive force was approximately 60 cycles per second. The field strength of the silent electric discharge within the reaction zone was 100,000 volts per centimeter. The residence time of the reaction mixture within the field of the silent electric discharge was approximately 8 seconds. On analysis of the effluent from the silent electric discharge apparatus, it was found that a significant quantity of phenol representing approximately 50 per cent of the total reaction product, was formed. In addition minor amounts of biphenyl, diphenylether, and phenoxy phenols were found to have formed.

EXAMPLE II

Example I is substantially repeated with the exception that toluene is used as the aromatic hydrocarbon. In this experiment, the principal product is a mixture of cresols. The principal by-product of the reaction is benzyl alcohol with small amounts of alkylbenzenes and other aromatic hydrocarbon being also formed.

EXAMPLE III

Example I is repeated with the exception that n-propylbenzene is used as the aromatic hydrocarbon. The principal product is a mixture of propylphenols with significant amounts of phenylpropyl alcohols also being found in the reaction product.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a phenol which comprises subjecting a gaseous mixture of an aromatic hydrocarbon and a free-oxygen-containing gas to a silent electric discharge.

2. A process according to claim 1 wherein the process is carried out at a temperature of less than 600°F and at a pressure within the range of 1 mm Hg to 100 psig.

3. A process according to claim 1 or 2 wherein the oxygen of the oxygen-containing gas and the aromatic hydrocarbon are in a molar ratio of 0.1:1 to 10:1.

4. A process according to any of the preceding claims wherein the frequency of the silent electric discharge is within the range of 30 cycles to 2 megacycles per second.

5. A process according to any of the preceding claims wherein said mixture contains approximately equimolar quantities of aromatic hydrocarbon and oxygen.

6. A process according to any of the preceding claims wherein the aromatic hydrocarbon is benzene.

7. A process according to any of the preceding claims wherein the electrical field strength of the silent electric discharge is within the range of 20,000 to 150,000 volts per centimeter.

8. A process according to any of the preceding claims wherein the residence time of the reactants within the field of the silent electric discharge is within the range of 0.1 to 1000 seconds.

9. A process according to any of the preceding claims wherein the oxygen-containing gas is air, oxygen or an air-oxygen mixture.

10. A process according to claim 1 substantially as hereinbefore described with reference to any one of the foregoing specific Examples I to III.

11. A process according to claim 1 carried out substantially as described with reference to the accompanying drawing.

12. Phenols whenever prepared or pro-

duced by any of the processes hereinbefore
described and claimed.

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1 SHEET

COMPLETE SPECIFICATION
*This drawing is a reproduction of
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